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PHOTOACOUSTIC SPECTROSCOPY STUDY ON Tb^{3+} - Gd^{3+} -SAL COMPLEXES

Key words: PA spectra, rare earth, intermolecular energy transfer

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ABSTRACT

The photoacoustic spectra(PAS) of the coprecipitates Tb^{3+} - Gd^{3+} -Sal complexes are reported. With the increase of the concentration of Gd^{3+} ion, the PA intensity of complexes decrease firstly, then increase. It is indicated that the addition of the second rare earth ion Gd^{3+} changes the relaxation processes of the complexes. The changes of the fluorescence spectra turn out complementary to the PAS. The intramolecular energy transfer and the intermolecular energy transfer processes in coprecipitates are discussed.

INTRODUCTION

The addition of Y^{3+} or certain lanthanide ions (La^{3+} , Gd^{3+} , Tb^{3+} , Lu^{3+}) can considerably enhance the fluorescence intensities of the chelates of Eu^{3+} , Sm^{3+} and Tb^{3+} in solution. This type of fluorescence enhancement actually is an intrinsic fluorescence phenomenon named the 'co-fluorescence effect'^[1-5]. The co-fluorescence can be found in chelate suspensions and in a micellar environment^[3,5]. In an actual solution, there is no co-fluorescence enhancement because the long distance between the chelates makes intermolecular energy transfer impossible. In solid, especially in coprecipitates, the distance between chelates could be short enough to take intermolecular energy transfer. So, it is necessary to study the luminescence properties of the co-fluorescence systems in solid.

Photoacoustic spectroscopy (PAS) is a direct monitor of nonradiative relaxation channel after excitation and therefore it is the complement of the fluorescence spectroscopy^[6]. Energy transfer in rare earth chelates has been widely studied by fluorescence spectroscopy. But since the energy transfer is a nonradiative process, PAS has an advantage to reveal the detail process.

In this paper, the chelates Tb^{3+} - Gd^{3+} -Sal (Sal: salicylic acid) are prepared. Using PAS and fluorescence spectroscopy, the luminescence properties of Tb^{3+} influenced by Gd^{3+} and the relaxation processes in Tb^{3+} - Gd^{3+} -Sal are studied in depth from two aspects: nonradiative process and radiative process.

EXPERIMENTAL

(I) Preparation of the Complexes: $(Tb_{1-x}Gd_x)Sal_3$

Sal was dissolved in ethanol. The pH value of this solution was adjusted to 7 with 20% KOH ethanolic solution.

Tb_2O_3 was converted to $Tb(NO_3)_3$ by treatment with 1:1 HNO_3 . Solution of $Tb(NO_3)_3$ was prepared by dissolving in ethanol. Ethanolic solution of $Gd(NO_3)_3$ was obtained by the same way.

The complexes of $(Tb_{1-x}Gd_x)Sal_3$ ($x=0.0, 0.3, 0.5, 0.6, 0.8, 0.9, 1.0$) were prepared by mixing the solution of Sal, $Tb(NO_3)_3$ and $Gd(NO_3)_3$ in proportion. The mixture was heated on a water bath at $70^\circ C$ and stirred under $pH=6-7$. The white crystalline were filtered, washed with ethanol and dried in vacuum drier under $30^\circ C$. Using the same way, the complexes of $(Tb_{1-x}Eu_x)Sal_3$ were prepared.

(II) Spectroscopic Measurements

The infrared spectra were measured as KBr pellets on MAGNA IR-750 spectrometer. According to IR spectra results, it is concluded that the carboxyl ($-COO^-$) is coordinated with Ln^{3+} by monodentate. Ln^{3+} is coordinated with three Sal by $Ar-COO^-$ and $Ar-OH$.

The PA spectra were measured on a single-beam PA spectrometer constructed in our lab^[7].

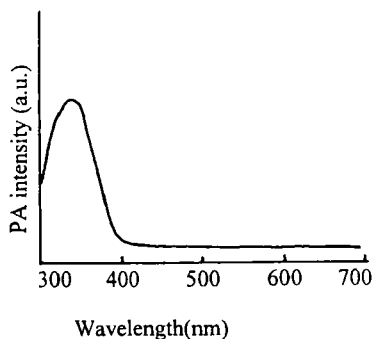
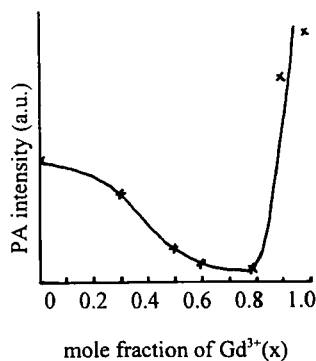
The fluorescence spectra were taken with the HITACHI 850 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

1. Photoacoustic spectra

The PA spectra of $(Tb_{1-x}Gd_x)Sal_3$ are shown in Fig.1. The broad PA absorption band at 340nm is assigned to $\pi-\pi^*$ transition of Sal. With the change of x (mole fraction) in the complexes, the location of the PA band hardly changes, but the PA intensity changes correspondingly. These changes of the PA intensity of the $(Tb_{1-x}Gd_x)Sal_3$ are recorded in Fig.2. With the increase of the concentration of Gd^{3+} , the PA absorbency of Tb^{3+} - Gd^{3+} -Sal complexes decrease. When eighty percent of Tb^{3+} in $TbSal_3$ are substituted by Gd^{3+} , the PA absorbency become the weakest (at 340nm). Then, the PA intensity increase rapidly. When all Tb^{3+} in $TbSal_3$ are replaced by Gd^{3+} ($GdSal_3$), the PA absorbency become the strongest.

The photoacoustic signal is obtained by detecting the heat generated through the nonradiative relaxation released by the sample. In the relaxation processes of

Fig.1 PAS of $(\text{Tb}_{0.9}\text{Gd}_{0.1})\text{Sal}_3$ Fig.2 Effect of Gd^{3+} on PA intensity

some samples, there are radiative processes (fluorescence spectroscopy) besides nonradiative processes(PAS). The PA signal of fluorescence complexes which relax by radiative process partly will be relatively weak^[8]. For $(\text{Tb}_{1-x}\text{Gd}_x)\text{Sal}_3$ complexes, the PA signal changes with the addition of the second rare earth ion Gd^{3+} . It is indicated the relaxation processes of these complexes make corresponding changes. So the fluorescence properties will change correspondingly.

2. Fluorescence spectra

The shapes of the fluorescence spectra of $(Tb_{1-x}Gd_x)Sal_3$ complexes are almost same. In Fig.3, only $(Tb_{0.2}Gd_{0.8})Sal_3$ complex's fluorescence spectra are shown. Fig.3a is the excitation spectrum ($\lambda_{em}=544nm$); Fig.3b is the emission spectrum where the excitation wavelength is fixed in the region of 340nm. In the emission spectrum, the five characteristic emissions of Tb^{3+} : $650nm(^5D_4 \rightarrow ^7F_2)$, $622nm(^5D_4 \rightarrow ^7F_3)$, $585nm(^5D_4 \rightarrow ^7F_4)$, $544nm(^5D_4 \rightarrow ^7F_5)$ and $490nm(^5D_4 \rightarrow ^7F_6)$ have been clearly observed. Among them, the emission at 544nm is the strongest.

The emission intensities (at 544nm) of $(Tb_{1-x}Gd_x)Sal_3$ complexes versus concentration of Gd^{3+} are shown in Fig.4. With the increase of Gd^{3+} , the fluorescence emission increases progressively. When eighty percent of Tb^{3+} in $TbSal_3$ are replaced by Gd^{3+} , the fluorescence become the strongest. Then, with the further increase of Gd^{3+} , the fluorescence emission decreases quickly. Fig.4 and Fig.2 are mutually complementary.

3. Energy transfer process in complexes

(1) Intramolecular energy transfer

From the fluorescence spectra it can be seen that the excitation spectrum is a broad band. As the main absorption bands of Tb^{3+} are at 284nm, 351nm, 368nm, 487nm and all sharp, the band at 340nm in excitation spectrum is due to the absorption of the ligand Sal. It means there may be energy transfer processes between Tb^{3+} and Sal. The luminescence of Tb^{3+} are sensitized by Sal.

The excited energy level (5D_4) of Tb^{3+} is at $20.4 \times 10^3 cm^{-1}$; The triplet state (T_1) of Sal is at $23.7 \times 10^3 cm^{-1}$. According to Dexter's theory^[9], the suitability of the energy gap between the resonance energy level of Ln^{3+} and the triplet state of ligand is a critical factor for efficient energy transfer. If the energy gap is too big, the energy transfer rate constant will decrease due to the diminution in the overlap between donor and acceptor. If the energy gap is too small, the efficiency of energy transfer will decrease because of the thermal deexcitation process. The

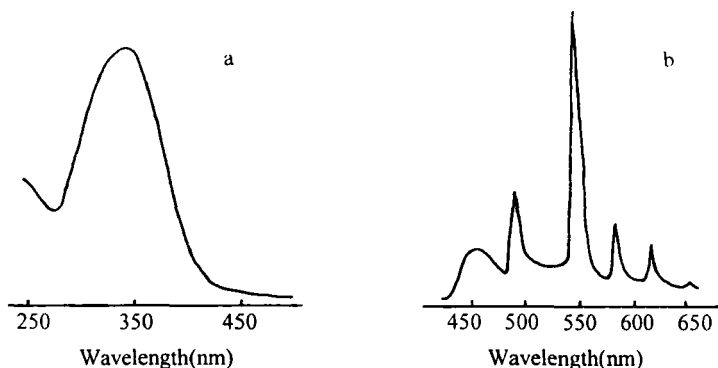


Fig.3 Fluorescence spectra of $(\text{Tb}_{0.2}\text{Gd}_{0.8})\text{Sal}_3$

a. Excitation spectrum($\lambda_{\text{em}}=544\text{nm}$)

b. Emission spectrum($\lambda_{\text{ex}}=340\text{nm}$)

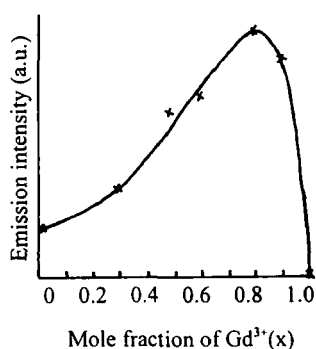


Fig.4 Effect of Gd^{3+} on emission intensity of Tb^{3+} (at 544nm)

energy gap between Sal and Tb^{3+} ($^5\text{D}_4$) is 3300cm^{-1} . It is suitable for energy transfer. So, the excited energy at T_1 is transferred by intramolecular energy transfer to the resonance level $^5\text{D}_4$ of the emitting ion Tb^{3+} . After that, Tb^{3+} undergoes a radiative transition resulting in a characteristic line-type emission of Tb^{3+} .

(2) Intermolecular energy transfer

Considering Foster^[10] and Dexter^[9] theories, energy can be transferred to molecules in short distance by intermolecular energy transfer. The efficiency of

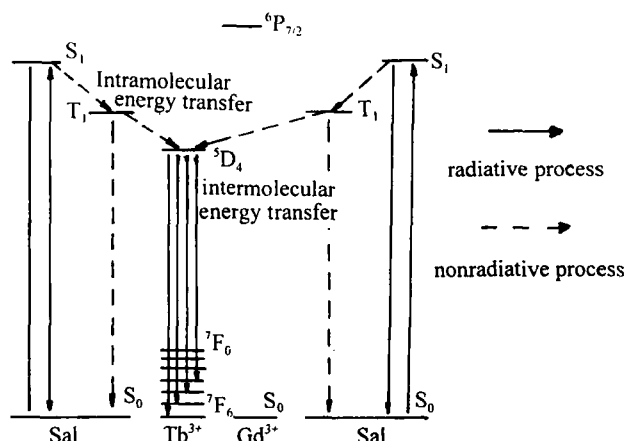


Fig.5 Intramolecular energy transfer processes and intermolecular energy transfer processes of $(Tb_{1-x}Gd_x)Sal_3$

the intermolecular energy transfer is dependent on close approach or contact of donor to acceptor. For the system studied, $(Tb_{1-x}Gd_x)Sal_3$ complexes are prepared by coprecipitation. The short distance between molecules in coprecipitate makes intermolecular energy transfer possible. The electron configuration of Gd^{3+} is $4f^7$. The excited levels of Gd^{3+} situate above the excited triplet level of Sal. Hence, the intramolecular energy transfer can not take place and no radiative excited-state deactivation processes exist within the $GdSal_3$ complexes. The excited energy at the ligand triplet state that can not be transferred to Gd^{3+} would be gathered. So $GdSal_3$ could be a donor and become the enhancing chelates. The stabilized triplet state of $GdSal_3$ transfers the energy by intermolecular energy transfer to the nearby chelates $TbSal_3$ (acceptor) in the aggregated particles, thus producing a considerably enhanced luminescence intensity of Tb^{3+} .

The energy transfer processes of $(Tb_{1-x}Gd_x)Sal_3$ are illustrated in Fig.5.

After eighty percent of Tb^{3+} in $TbSal_3$ are substituted by Gd^{3+} , the luminescence intensities of Tb^{3+} decrease because of the excessive reduction of the acceptor.

Experiment results indicate that the fluorescence enhancement phenomenon can not be found in the mixture of TbSal_3 and GdSal_3 in any proportion. As the mixture is gained in a mechanical way, the distance between molecules is too far to take energy transfer processes.

For Tb^{3+} - Eu^{3+} -Sal systems, the results are different from $(\text{Tb}_{1-x}\text{Gd}_x)\text{Sal}_3$ complexes. The fluorescence intensity of Tb^{3+} can not be enhanced by Eu^{3+} . This is due to the excited levels ($^5\text{D}_2$ and $^5\text{D}_1$) of Eu^{3+} below the excited triplet level of Sal. The excited energy of Sal may be transferred to these levels and then fall rapidly to the ground state through nonradiative deactivation processes. These deactivation processes make EuSal_3 can not be a donor and the fluorescence enhancement can not take place.

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